OPTIMIZATION OF ALUM COAGULATION FOR THE REMOVAL OF TANNINS FROM NATURAL WATERS

A Thesis Submitted
In Partial Fulfilment of the Requirements
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MASTER OF TECHNOLOGY

By
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DEPARTMENT OF CIVIL ENGINEERING
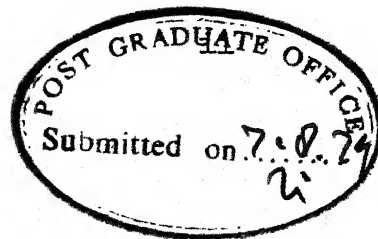**INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**
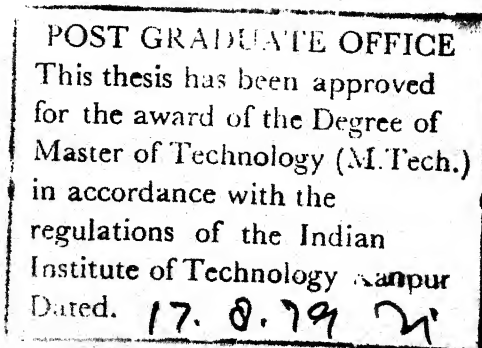August, 1979

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CERTIFICATE

Certified that the work presented in this
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the Removal of Tannins from Natural Waters' by Shri
Kurmala Venkata Kasi Visweswara Rao has been carried
out under our supervision and it has not been
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CONTENTS

ABSTRACT

In an attempt to assess the water treatment plant for the tannin removals, it has been found that the natural turbidity has a high potential to adsorb tannins. Tests with natural river water with a turbidity of 140 N.T.U. gave about 90 to 95 percent removal of tannins. Alum coagulation seemed to be very effective in removing tannin loaded turbidity. The dose of alum decreases with the increasing initial turbidity. Tannin removal is affected during summer seasons because of the low turbidity. In order to overcome this, higher doses of alum is required to produce metal hydroxide precipitate on which tannins can adsorb. It has also been observed that the alum coagulation employed to remove the tannin loaded turbidity is dependent upon Gt-factor. The optimum Gt-factor for maximum removal of tannins appears to be independent of initial tannin concentration in the raw waters. However, the optimum 'Gt' value rapidly decreased with the increase of raw water turbidity. The Gt-factor value of about '1000' was found to be sufficient at a turbidity of 125 N.T.U. whereas a value of about 10,000 or even more is required in case of 15 N.T.U. turbidity for the same tannin removal. Interior penalty function method, a nonlinear programming technique, was used to optimize the influencing parameters, viz., velocity gradient, time of flocculation alum dose and alkalinity. This method can provide information for the optimal design of the coagulation and flocculation unit for maximum tannin removals.

LIST OF FIGURES

1. INTRODUCTION

Water, besides being a fundamental requirement for the existence of life, serves as an extremely important raw material for many industries. Industrialization is very important for modern civilized life. It had grown from basic industries like textile, paper to the modern electrical, electronic industries meeting the timely demands of the society.

For centuries, the use of leather has been very popular for many purposes starting from the manufacture of footware. The tanneries tan the skin of dead animals to produce the leather. Vegetable tanning process is most commonly followed in all the tanneries. Tannins, a group of organic compounds widely distributed in plants, are utilized in this vegetable tanning process. The tannery effluents create pollutional problems when discharged into river water and consequently attracted the attention of environmental engineers.

Chakrabarty et.al. (1965) clearly explained that though the tannery wastes produced by industries located in Kanpur do not constitute a significant part of the municipal wastes, the pollution load contribution is very significant. Tannery wastes in Kanpur are 1.6 percent of the total city wastes but their contribution to the 5-day Biochemical Oxygen

Demand (B.O.D.) value is about 30 percent. Thus the tannery wastes are approximately equivalent to the wastes produced by 0.23 million people on the basis of B.O.D. contribution.

The textile and paper industries are most affected by the presence of tannins in the raw waters. Tannins impart an yellowish tinge to the product which is highly undesirable especially in case of white or delicate shades. Since the colour of the product is an essential factor determining the quality of the product, these industries do experience heavy losses due to the inferior quality of the product.

Although many researchers worked on the treatment of tannery wastes, very few evaluated the tannin removals in the proposed treatments which is a very important parameter for the down stream industries. Working on removal of tannins from river waters Venkitachalam (1972) evaluated chlorination, ion exchange and adsorption processes. Chlorination at high doses gave maximum removals but it could not be put into practice due to the presence of high residuals which in turn are to be removed by adopting yet another process. Adsorption with animal charcoal or activated carbon/also observed to be was efficient for tannin removal. However the proposed treatment processes are costly. Surprisingly no work has been reported on tannin removals in conventional water treatment plant.

Hence, a study is to be carried out to evaluate the conventional water treatment system for tannin removal. The

present study attempts to evaluate the potential of coagulation for removal of tannins. After understanding the mechanism of tannin removal, it is possible to suggest certain process modifications for the existing water treatment plant with a nominal increase in the cost.

Utilising the latest mathematical techniques like optimization methods, it is possible to optimize various parameters controlling the alum coagulation for maximum tannin removals. In the present investigation an attempt is made in this direction. The relationships between different parameters and tannin removals can be conveniently determined by simple laboratory experiments.

2. LITERATURE REVIEW

2.1 Introduction:

Prior to heading in the direction of achieving the objective of tannin removal from natural waters, it is very essential to have some knowledge about the tannins, tanneries, tannery wastes and the actual problem faced due to the presence of tannins in the raw waters. The basic literature available in regard to the treatment of tannery effluents before their disposal and treatment of tannin containing river water was considered to be the invaluable information for an understanding of the mechanism of tannin removal.

Prior to embarking on the removal of tannins, it is highly desirable to know what tannins are and their beneficial uses and deletereous effects.

2.2 Tannins:

The tannins are a group of organic compounds widely distributed in plants, abundent in bark while being also seen in leaves, roots and fruits (Cochvane, 1958). They are described as a mixture of derivatives of polyhydroxy benzoic acids and occur in substances of vegetable origin like sumac, gally nuts, myrobalans, root bark, chinese tea etc. These tannins are very well-known for centuries for their ability to tan skins. A solution of tannic acid will precipitate 'Albumen' (Rose et.al., 1948).

Rose et.al. worked out an approximate formula for tannins, viz., $C_{14}H_{10}O_9$ while Cochrane (1958) gave the basic molecular structure of tannins.

The barks, leaves, roots and fruits which constitute a major source of tannins are listed below.

1. Barks : Wattle, Mangrove, Oak, Eucalyptus, Pine, Larch, Willow, Gum tree

2. Leaves : Sumac, Gambier

3. Roots : Canalgre, Paluette

4. Fruits : Divi-Divi, Tara, Valonia

2.2.1 Important properties of Tannins:

A tannin is a lustrous and faintly yellowish amorphous powder. It is an odourless spongy mass possessing strong astringent taste. The melting point was observed to be 210°C. It is soluble in water, alcohol and acetone and are almost insoluble in benzene, chloroform, ether and petroleum.

2.2.2 Beneficial industrial uses:

The tanning industry is an industry utilizing a maximum percentage of tannins extracted. Tannins are also

used in the manufacture of various chemicals viz., tannates, gallic acid, pyrogallic acid and hydrosols of noble metals, textiles as mordant and fixative, galvano plastics, inks, certain pharmaceuticals, paper for sizing and mordant for coloured papers, stove polishing compounds, etc. Besides, tannins are used in photography, as a corrosion preventive chemicals in boiler water, in electro-plating, as substitutes for rubber, in the deodourization of crude oil, as a clarification agent in the wine manufacture and brewing, and for improvement of high temperature properties in nylon industry.

2.3 Pollution of Natural Waters by Tannery Effluents:

Venkitachalam (1972), rightly, pointed out that the presence of tannins in natural waters is mostly due to the discharge of untreated tannery effluents from leather tanning industry into the natural waters. Reports of Chakrabarty et.al. (1964, 1965) clearly reveal the gravity of the problem due to various tanneries discharging their wastes directly or indirectly without any treatment into the river Ganga near Kanpur. It was clearly pointed out that various ill-effects could be observed in Ganga waters as well as in a nearby rayon industry drawing water from the river Ganga at a point downstream due to the presence of tannins in the waters. The rayon industry, despite having a well maintained water treatment plant, is not able to obtain water free from tannins.

Ajwani (1962) in his report on a survey conducted in Bombay, has described the problems caused by the disposal of waste effluents from the tanning vats into the natural waters. Significant damage to aquatic life is one of the important damages reported i.e. tannins are very much responsible for the depletion of oxygen in the stream waters after the waste effluents entered the natural waters. At a glance, the problems of polluted waters containing tannins have to be given a serious thought in order to restore the quality of the water making it fit for downstream industries.

2.4 Tanneries Near Kanpur City, Their Waste Characteristics and Treatment:

A layout of the tanneries near Kanpur is shown in Figure 2.1. A majority out of nearly thirty tanneries in Uttar Pradesh State (Chakrabarty et.al., 1965) are located in Kanpur. Most of the Kanpur tanneries are situated in Jajmau, about eight miles east of Kanpur city. The city has a few tanneries scattered over different areas, with sizes, production capacities and waste volumes larger than those of the tanneries at Jajmau. All the 22 tanneries in Kanpur operate vegetable tanning process in the purification of animal hides to get leather. The number of hides processed per day being in between 25 and 600. The effluents from the tanneries are intermittently discharged into a 1067 mm diameter sewer which is exclusively meant for carrying the

Fig. 2·1 Location of tanneries near Kanpur
(Printed after Venkitachalam, 1972)

effluents to the city's sewage pumping station about 2 miles away downstream where the effluents are mixed with the city sewage carried through a separate 2286 mm diameter sewer, and are partly utilized in the nearby sewage farm and the rest disposed of into the river Ganga.

Amongst various units of a tannery, the wastes from the tanning vats are the strongest of all the wastes having a Chemical Oxygen Demand (C.O.D.) of about 15,000 mg/l and suspended solids concentration of 20,000 mg/l. These waters are brown in colour with offensive odour. The character-istics of effluents from various leather processing units of a tannery, processing about 100 hides per day is shown in Table 2.1.

2.5   Problem Faced by Downstream Industries Due to the Presence of Tannins in Raw Water:

Due to the presence of tannins in the process water for manufacture of clothes including rayon,   paper etc., the product is being imparted an yellowish tinge degrading the quality of the product, thus causing heavy losses to the industry. A clear examination of the tolerance limits of water for the textile industry (IS 201, 1964) given in Table 2.2 reveals that the white and delicate shades require very high quality water particularly in regard to colour (maximum permissible limit of 5 Hazen units). Hence it is very essential to study the removal of tannins by careful

Table 2.1

All Units Except for pH are in mg/l (Dasnurkar, 1968)

Waste source	Tannins	C.O.D.	B.O.D.	Total solids	Suspended solids	pH	Alkalinity	Chlorides
Soaking pits	–	960	780	4900	2240	8.2	520	12600
Liming pits	–	8000	6400	39400	14700	11.1	4800	90
Deliming vats	–	1400	840	3400	820	8.6	800	80
Tanning vats	6400	15600	9600	72900	22500	5.5	200	–
Composite wastes	1200	4800	3600	23000	15800	8.9	1600	2800

Table 2.2

Tolerances for Water for Textile Industry (IS 201-1964)

Corrosivity: The water should be non-corrosive. The suggested test is with treatment with calcium carbonate. Increase in pH or alkalinity indicates the corrosivity.

Algae and Mould Spores: The water should be free from algae and mould spores (Test as per IS 62

Odour: The water should be free from objectionable odour.

Sr. No.	Characteristic	Tolerances for		
		General purposes	Bleaching, dyeing and subsequent processing	Wool scouring
1.	Colour (Hazen Units), max	20	5 (see Note 2)	70
2.	Turbidity (Silica Scale Units), max	5	5	-
3.	pH	6.0 to 8.5	6.0 to 8.5	6.0 to 8.5
4.	Total hardness (as CaCO₃), mg/l, max	50 (see Note 2)	50	50
5.	Iron (as Fe), mg/l, max	0.25	0.25	0.25
6.	Manganese (as Mn), mg/l, max	0.1	0.1	0.1
7.	Iron (as Fe), and Manganese (as Mn) added together, mg/l, max	0.25	0.25	0.25

Note 1: When dark or medium dark dyeing is done, a relaxed maximum limit of 20 may be permissible but for whites and delicate shades, the limit of 5 shall not be relaxed.

Note 2: For processes which are not sensitive to hardness salts or where internal sequestering agents are used, a maximum limit of 200 is permissible.

manipulation of water treatment in order to minimize the deletereous effects damaging the output from the industries of textiles, paper etc.

2.6 Treatment of Tannery Wastes:

Appreciation of the harmful effects of discharging untreated tannery wastes into the natural water bodies dates back to 1951 when Thorstensen described in detail the gravity of the problem. He was followed by a horde of environmental engineers suggesting various types of treatments so that the pollution hazard due to the presence of tannins in the natural waters becomes insignificant.

2.6.1 Sedimentation:

According to Howalt (1928), Fales (1929), about 50 percent B.O.D. removal and about 80 percent removal of suspended solids can be attained by plain sedimentation. Harnley et.al. (1940) showed 63 percent B.O.D. removal with Dorr-Oliver clarifier. Scholz attempted to neutralize the wastes with flue gases prior to the sedimentation to observe about 80 percent B.O.D. removal. Bramschweig (1962) and Marshal (1951) came to the conclusion that pH control did not improve sedimentation characteristics and hence was unnecessary.

2.5.2 Chemical coagulation and flocculation:

Alum was reported (Dular, 1954; Kubelka, 1957) to be the best chemical for coagulation of both vegetable and chrome

tanning wastes. Munteanu (1963) reported 80 percent removal
of B.O.D. at a dose of 500 mg/l of alum. Many other workers
also agreed that this is the best possible treatment for
tannery wastes. Dasnurkar (1968) observed 52 percent removal
of tannins in case of composite wastes using 'Alum' as the
coagulant. While ferric chloride was employed as the
coagulant, the removal of lining wastes was reported to be
71 percent.

2.6.3 Biological treatment:

In the activated sludge process,   tannery
wastes were mixed with municipal wastes in a ratio of about
1 : 10. Warren et.al. (1936) found this process to be
efficient and hence suitable. At a loading rate of 100 lb/
day/1000 cft. aeration capacity, the activated sludge process
showed a removal of 95 percent in B.O.D. after a pretreatment
to lessen the pH (Rosenthal, 1959).

2.6.4 Review:

One main feature from the above literature can be
readily observed/that no body except Dasnurkar (1968) gave
any data on tannin removal which has to be considered very
important in view of pollution of natural waters by tannins.
Dasnurkar mentioned about 90 percent tannin removal and about
87 percent C.O.D. removal in activated sludge process when
the tannery wastes and municipal wastes were mixed in the
ratio 1 : 9.

From the observations of Dasnurkar (1968), it can be concluded that tannin removal will be quite significant if there is significant B.O.D. or C.O.D. removals. Hence the author feels that any sort of treatment given to the tannery wastes before their disposal into natural waters helps in reducing the pollutional load on the water treatment plants of downstream industries.

2.7 Treatment of Natural Waters Containing Tannins:

In spite of the efficient waste treatment to reduce the tannin concentration, some of it is expected to be present in the river waters. In order to avoid the dele-terious effects of tannins on industrial product, the industrial wastes treatment plant should aim at removing these tannins and keep them within the tolerance limits. In the present section, efforts made by various investigators are presented.

Coagulation by alum accompanied by the anionic polyelectrolyte 'Nalcolyte 675' was found to be a fruitful method to combat with the colour problem caused by the con-centrations of tannins. More than 90 percent colour removal was reported at a pH of 7.0 (Venkitachalam, 1972). Tomlison (1970) used only polyelectrolyte 'Nalcolyte 605' at a controlled pH of 3.0 and reported similar removals with about 30 mg/l dose of the polyelectrolyte.

Many other scientists reported to have used 'ion exchange' and 'activated carbon' adsorption systems in the treatment of natural waters for industrial purposes as well as in water reclamation from wastewaters. However, no data on the tannin removals from river waters containing low tannin concentrations has been reported except by Venkitachalam (1972).

Venkitachalam reported tannin removals from natural waters by (a) ion exchange using various ion exchange resins (b) adsorption using animal charcoal and granular activated carbon and (c) chemical oxidation using chlorine. The ion exchange process was reported to have yielded 40-45 percent removal before the occurrence of tannin breakthrough at 200 litres of water treatment. High removals of tannin were observed with physical adsorption of tannins on to the animal charcoal. About 86 percent tannin removal was reported with fixed bed grannular carbon adsorption system. Higher doses of chlorine (greater than about 60 mg/l) resulted in 90-95 percent tannin removals but this poses a problem of removing high residual chlorine.

2.8 Summary:

Chlorination which was declared as the best method cannot be practised because of the problem of removing residual chlorine by another unit process and hence costly. Next to it, animal charcoal adsorption seems to be a better

alternative. In this case, the tannin molecules are adsorbed almost instantaneously on high doses of animal charcoal. This is due to the large surface area provided by the adsorbent for sorption of tannins. Tannin molecules try to diffuse into the milli or micro pores of the adsorbent or to attach themselves to the adsorbent and this should give clue to employ cheap, readily available sorbents which present a very large surface area for sorption of tannins.

It is well-known that the clay particles contribute to the turbidity in the river waters to a maximum extent. Clay particles, which possess a lot of micropore spaces, can be conveniently used for the tannin-adsorption. Hence certain alterations to the existing water treatment plants can be proposed in which case there will be a nominal increase in the cost while accounting for tannin-removals from natural waters. Amongst all the convenient units of a water treatment plant, coagulation and flocculation unit seems to be best suited when we can readily remove tannin-loaded turbidity using any efficient coagulant since the tannin-adsorption is believed to be the physical adsorption (Venkitachalam, 1972) wherein the process is not very much dependent on time.

3. SCOPE OF INVESTIGATION

3.1 General Objectives of the Present Study:

The present study is planned to fulfil the following objectives.

(a) To evaluate the potential of naturally occurring turbidity and to remove tannins from natural waters as against commercially available sorbents.

(b) To evaluate the potential of alum coagulation and flocculation in removing tannin loaded turbidity.

(c) To optimize all the variables influencing the tannin removals from natural waters by coagulation using alum. This is expected to yield information regarding the optimal conditions for maximum removal of tannins viz., alum dose, time of flocculation etc.

3.2 Proposed Experimentation:

In order to fulfil the above objectives, the investigation is proposed to be carried out in the following lines.

(i) The tannin sorption potential of natural turbidity is to be investigated using conventional jar test without the addition of coagulant.

(ii) The removal of tannin loaded turbidity is to be investigated using alum coagulation and flocculation.

(iii) In order to evaluate the effect of/ ^Gt-factor on tannin and
turbidity removals, tests are conducted at different
speeds for different times of flocculation. This
would yield optimum 'Gt' factor, a dimensionless
parameter used in the design of flocculators.

(iv) An optimum combination different parameters contri-
buting to maximum tannin removals is obtained by using
an appropriate optimization technique. In case of
present work, nonlinear programming algorithm is
planned to solve the formulated optimization problem.

4. MATERIALS AND METHODS

In order to fulfil the objectives, investigations were carried out using appropriate methods. The mathematical formulation of the optimization problem also require the generation of data on tannin removals by turbid particles present in water and removal of tannin loaded turbidity by alum coagulation and flocculation.

4.1 Materials:

4.1.1 Tannins:

Tannic acid manufactured by W.J. Bush & Co. Ltd., London, was used as the source for tannins. The test water was prepared by adding tannins, just before experimentation to the tap water containing bentonite turbidity. In some experiments the lower ganges water was treated as test water for tannin removal. The characteristics of the tap water and natural river water (of river Ganga) are presented in Table 4.1.

While determining the tannin removals, it has been necessary to estimate the concentrations of tannins at different times. Tannins reduce tungstophosphoric and molybdophosphoric acids to produce a blue colour suitable for the estimation of concentrations upto about 10.0 mg/l of tannic acid. This colour can be conveniently measured using a

spectrophotometer (Spectra 950, Neotronics Corporation, Bombay). The method of estimation was according to the Standard Methods (1975). The calibration curve for tannins is presented in Figure 4.1.

Table 4.1

Average Characteristics of Ganges Water and I.I.T. Kanpur Tap Water

Characteristics	Concentration in	
	Ganges water	Tap water of I.I.T.
pH	8.2	8.5
Turbidity	140.0 N.T.U.	Not detectable
Total alkalinity (as $CaCO_3$)	190.0 mg/l	405.0 mg/l
Total hardness (as $CaCO_3$)	120.0 mg/l	174.0 mg/l
Chlorides (as Cl^-)	18.0 mg/l	60.0 mg/l
Sulphates (as SO_4^{--})	38.0 mg/l	140.0 mg/l
C.O.D.	31.0 mg/l	Not detectable
Phosphate (as PO_4^{-3})	0.5 mg/l	–
5-day B.O.D. (at 20°C)	26.0 mg/l	–
Coliform count (MPN/100 ml)	280,000	< 1

Fig.4·1 Standard curve for tanning estimatio

4.1.2 Bentonite:

Bentonite clay was used to create artificial turbidity in the tap water as bentonite is more closer to natural water turbidity. The important properties of the 'bentonite' used in the study are listed below:

Specific gravity $\qquad$ = 2.58

Average particle diameter $\quad$ = 2.5 μ m

Total surface area $\qquad$ = 425.61 m^2/g

Characteristic based spacing = 15 $\overset{\circ}{A}$

Cation exchange capacity $\quad$ = 45 meq/100 g

Approximate composition : Montmorillonite: 70%

$\qquad\qquad\qquad\qquad\qquad\qquad\quad$ Felspar $\qquad$: 20%

$\qquad\qquad\qquad\qquad\qquad\qquad\quad$ Calcite $\qquad$: 5%

$\qquad\qquad\qquad\qquad\qquad\qquad\quad$ Quartz and rest: 5%

Preparation of stock bentonite suspension: The preparation of stable bentonite clay suspension was as per Van Olphen (1963) method.

The bentonite clay suspensions which are to be employed as various turbidities should be stable. The following is the procedure for obtaining stable bentonite suspensions according to Van Olphen (1963).

Clay particle by definition should measure 2 μ m or less. To separate this fraction from the minerals ground in the ball mill, the minerals were suspended in a vertical cylinder for 12 hours.

The clay particles were suspended in the water by rigorous stirring for about 10 minutes at sufficiently high speeds using 'Remi' laboratory stirrer so as to keep the particles in suspension. The clay concentration was kept as high as possible. Then the suspension was diluted sufficiently to ensure gravity settling. As usually is the case all the clay samples were found to be contaminated with sufficient amounts of electrolytes and therefore there was flocculation and rapid settlement of minerals. The clear fluid was syphoned off and the clay was again redispersed in water by stirring. This procedure is repeated till the electrolyte concentrations were lowered below the flocculation value and the clay fraction stayed in the suspension owing to peptization. Peptization is the process of stabilization of clay suspensions by the reversal of the positive edge charge into a negative charge. It may be noted at this stage that excess concentrations of peptizing agents, on the contrary, promote flocculation. At this stage, the particles still settling rapidly be discarded as they formed impurities such as quartz etc. with diameters exceeding 2 μm.

4.2 Experimental Methods:

4.2.1 Conventional jar test:

Standard jar test apparetry (Phipps & Birn Inc., Richmond, Virginia, U.S.A.) was used to evaluate the sorption of tanning on the turbidity present in test and water and to

study the removal tannin loaded turbidity by alum coagulation
and flocculation. The effect of varying intensities of
mixing on removal of turbidity is also studied using the
method. It has been assumed that this would be quite
meaningful and can/be extended to the practical treatment unit trans-
ferring properly the flesh mixings, velocity gradients, times
of flocculation. The schedule of a standard jar test is as
below.

Flash mixing	01 minute	100 rpm
Flocculation	20 minutes	30 rpm
Sedimentation	30 minutes	

At the end of sedimentation time samples were carefully drawn
for the analysing residual turbidity (Hach Turbidmeter, Model
2100, Hach Chemical Company, U.S.A.) and tannin concentration
according to Standard Methods (1975).

4.2.2 Jar tests to study the adsorption of tannins on natural turbidity:

To different beakers containing water having a
turbidity (of Ganga water equal to 140 N.T.U.), known concen-
trations of tannins were added to be natural turbid waters
each time. The samples were subjected to conventional jar
test with a modified speed of 60 rpm for 20 minutes. The
sample was centrifuged at 10000 rpm in a Sorvall Centrifuge
(S-S-3 automatic superspeed centrifuge, Ivan Sorval Inc.,
U.S.A.) to spun down the sediment and the clear supernatant

was subjected to estimation of tannins. The same procedure was followed for studying the sorption of tannins on the artificial turbidity provided by bentonite in tap water.

4.2.3 Jar tests to study the removal of tannin loaded turbidity by alum coagulation:

A series of standard jar tests were conducted using varying concentrations of tannin and turbidity. In these, instead of centrifugation, alum (a laboratory reagent, $Al_2(SO_4)_3.16 H_2O$) coagulation was used to remove the tannin loaded turbidity. Optimum alum doses for each combination were obtained. The tannin and turbidity residuals after the tests were also estimated.

4.2.4 Jar tests varying Gt-factor:

To obtain the effect of different mixing intensities defined by velocity gradient, G, on tannin and turbidity removals by tests were conducted with varying the speeds of flocculation (5, 10, 20, 50, 80 and 100 rpm) and times of flocculation (0, 5, 7, 10, 15 and 20 minutes) for different known turbidities (15, 50, 125 N.T.U.) and tannin concentrations (5, 10, 15 mg/l).

4.3 Theoretical Methods:

4.3.1 Lagrangian interpolation Method (Ralston, 1965):

According to 'Standard Methods', the Beer's law may not be valid in case of tannin detection after, say, a

concentration of 6 mg/l. But it can still be assumed that the light penetration is a measure of the concentration though it may not be in the direct proportion. Hence the data points of the calibration curve are used to predict the concentrations from the readings of absorbance whenever there was a need to detect the tannin concentration by 'interpolation method'. For simplicity and reasonable accuracy, Lagrangian method of interpolation is adopted. At the same time the error in drawing a graph is eliminated and the time consumed in finding the ordinate value from the required abscissa could be almost eliminated. The principle and working of the method is illustrated below briefly.

Let there be n points in a graph whose co-ordinates are (a_1, y_{11}), (a_2, y_2), ... (a_n, y_n). Assuming a function $P(x)$ as the polynomial function to obtain the ordinate for a given abscissa value, first two points viz., (a_1, y_1), (a_2, y_2) are initially considered.

$P(x)$ given abscissa ordinate to be found.

Now $P(x)$ can be written as follows:

$$P(x) = \frac{y_1(x - a_2)}{(a_1 - a_2)} + \frac{y_2(x - a_1)}{(a_2 - a_1)}$$

i.e.

$$P_{a_1 a_2}(x) = \frac{1}{a_2 - a_1} \begin{vmatrix} y_1 & (a_1 - x) \\ y_2 & (a_2 - x) \end{vmatrix}$$

And
$$P_{a_1 a_3}(x) = \frac{1}{a_3 - a_1} \begin{vmatrix} y_1 & (a_1 - x) \\ y_3 & (a_3 - x) \end{vmatrix}$$

$$\vdots$$

$$P_{a_1 a_n} = \frac{1}{a_n - a_1} \begin{vmatrix} y_1 & (a_1 - x) \\ y_n & (a_n - x) \end{vmatrix}$$

These $P_{xx}(x)$'s replace y's in the determinent when third point (or a next point) is taken into the consideration. And the procedure is repeated till all the points are covered. Final $P_{xx...x}(x)$ look like:

$$P_{a_1 a_2 ... a_n}(x) \qquad \frac{1}{a_n - a_{n-1}} \begin{vmatrix} P_{a_1 a_2 ... a_{n-1}}(x) & (a_{n-1} - x) \\ P_{a_1 a_2 ... a_{n-2} a_n}(x) & (a_n - x) \end{vmatrix}$$

$$... (4.1)$$

Equation 4.1 gives the value of the ordinate $P_{a_1 a_2 ... a_n}(x)$ for the given abscissa 'x' considering all the given 'n' data points.

Since this method is very easily programmable, it has been used successfully in predicting the concentration of the tannins after each experiment using the computer. This has been also used in predicting the final tannin residuals, hence the tannin removals after obtaining the optimum alum dose and other conditions from the optimization algorithm.

4.3.2 Least square method or regression analysis (Pennington, 1965):

To assign an equation to the data points, this method is easy and convenient. The basic principle and working is illustrated here in a brief manner.

Principle: When we assign an equation, it can be assumed in case of linear regression as

$$c_1 f_1(x_1) + c_2 f_2(x_1) + \dots + c_m f_m(x_1) = y_1$$

$$\vdots$$

$$c_1 f_1(x_n) + c_2 f_2(x_n) + \dots + c_m f_m(x_n) = y_n$$

Hence the deviations δ_j (j = 1 to n) can be calculated as follows.

$$\sum_{i=1}^{m} c_i f_i(x_j) - y_j = \delta_j \qquad j = 1, 2, \dots, n$$

$$\dots (4.2)$$

and we desire to choose the c_i's such that

$$\sum_{j=1}^{n} \delta_j^2 = \text{minimum}$$

Working: A necessary condition for it to be minimum is that its partial derivatives by each of the c_i's must vanish i.e.,

$$\frac{\partial}{\partial c_k} \sum_{j=1}^{n} \delta_j^2 = 0 \qquad \text{for } k = 1, 2, \dots m$$

or
$$\sum_{j=1}^{n} \frac{\partial}{\partial c_k} \frac{\partial \delta_j}{\partial c_k} = 0 \qquad \text{for } k = 1, 2, \dots m$$

But
$$\frac{\partial \delta_j}{\partial c_k} = f_k(x_j)$$

Substituting this and the value of δ_j from Eq. (4.2),

$$\sum_{j=1}^{n} \left[\sum_{i=1}^{m} c_i f_i(x_j) - y_i \, f_k(x_j) \right] = 0 \quad \text{for } k = 1,2,\ldots m$$

or
$$\sum_{i=1}^{m} c_i \sum_{j=1}^{n} f_i(x_j) f_k(x_j) = \sum_{i=1}^{n} y_i \, f_k(x_j)$$

$$\text{for } k = 1,2,\ldots m$$

This is a system of 'm' linear equations with unknowns c_1, c_2, ... c_m and can be solved by any convenient method.

4.3.3 Optimization algorithm (Fox, 1971; Rao, 1978):

This is the widely known nonlinear optimization technique used extensively in many engineering optimization problems.

A general mathematical programming problem can be solved either by (a) direct methods in which the constraints are explicitly handled or by (b) indirect methods, in which the constrained formulation is transformed into a sequence of unconstrained optimizations. One main reason for the appeal of the sequential unconstrained formulation of the constrained optimization problem is that the sequential nature of the method allows a gradual approach to the criticality of the constraints. In addition, the sequential approach permits a graded approximation to be used in the analysis of the system.

One of the approaches to reduce the total computational time of automated optimization problems is to adopt a method which permits the use of approximate analysis without involving significant errors. The penalty function methods allow the use of approximate analysis during the various phases of optimization. Furthermore, the variable metric unconstrained optimization technique, discussed later, is inherently more stable and little effected by minor errors introduced through analysis approximations. It is for this reason that an optimization technique from the indirect methods was choosen for the present work.

(i) <u>Interior penalty function method</u>: Penalty function methods transform the basic problem into alternative formulations such that numerical solutions are sought by solving a sequence of unconstrained optimization problems. A penalty function $\emptyset(\vec{X}, r_k)$ would be formulated by adding a penalty term $G(g_1, g_2, g_3, \ldots)$ which is a function of the constraints, to the objective function $f(\vec{X})$ where this penalty function would be optimized for a sequence of response factors r_k. The penalty term suggested by Fiacco and McCormick (1964) is used in the present work as it being a simpler form amongst the various choices. In this formulation the penalty term is small at points away from the constraints in the feasible region, but it shoots up as constraints are approached. Then the actual optimization problem looks like

Minimize $\phi(\vec{X}, r_k) = f(\vec{X}) + r_k \sum_{j=1}^{m} \frac{1}{g_j(\vec{X})}$

for a decreasing sequence of r_k, $r_{k+1} < r_k$.

The penalty function is not defined if $\vec{X}$ falls in infeasible region. It is true that without any starting point, by a sequence of iterations, a good starting point can be arrived at. But since it is not difficult to find an initial feasible point at the expense of large value of the objective function $f(\vec{X})$ in many engineering problems. In the present work, a feasible point is given on the basis of the experience of the results of some experiments conducted.

Since each of the designs generated by this method lies inside the acceptable region of the design space, the method is classified as 'interior penalty function' method. The method tends to generate a sequence of designs which decrease the value of the objective function such that none of the designs in the sequence is critical with respect to the set of inequality constraints.

(ii) <u>Davidon-Fletcher-Powell (variable metric) unconstrained optimization method</u>: The selection of an efficient unconstrained minimization method is extremely important because a sequence of such minimizations of the penalty function $\phi(\vec{X}, r_k)$ are to be performed. A critical search of the unconstrained algorithms suggests to opt for gradient methods

as they are superior to non-gradient methods in the sense they use more information about the function (viz., gradients). The well-known most powerful D-F-P method is used in the present study.

Given a starting point $\vec{X}_o$ and a positive definite matrix H_o, this method finds the local minimum of $\emptyset(\vec{X}, r_k)$ by generating a sequence of X-vectors such that

$$\vec{X}_{i+1} = \vec{X}_i + \lambda^* \vec{s}_i$$

And
$$s_i = - \left[H_i \right] . \nabla \emptyset(\vec{X}_i)$$

where $\vec{X}_{i+1}$ is the design vector corresponding to the minimum of $\emptyset$-function along the current direction $\vec{s}_i$, $\vec{X}_i$, the starting design vector and λ^*, the optimum step length .

Prior to the beginning of the next cycle in the iteration, the matrix H is modified to take local characteristics of the $\emptyset$-function into account in order to avoid the zig-zag behaviour common to many other optimization techniques.

$$H_{i+1} = H_i + M_i + N_i$$

$$M_i = \lambda_i^* \frac{S_i \, S_i^T}{S_i^T \, Q_i} \qquad \text{and} \quad Q_i = \nabla f(\vec{X}_{i+1}) - \nabla f(\vec{X}_i)$$

$$= \nabla f_{i+1} - \nabla f_i$$

$$N_i = - \frac{(H_i \, a_i)(H_i \, a_i)^T}{Q_i \, H_i \, Q_i}$$

The stability is insured by preserving the symmetry and the positive definiteness of H_i while it is updated. The positive definiteness of the H_i matrix is influenced only by the accuracy with which λ^* is determined. So the data arising from a poor approximation of λ^* need not be taken into consideration while updating the H-matrix. Hence, whenever, $s_i^T \quad \emptyset_{i+1}$ is large (λ^* is poorly approximated), the one-dimensional minimization algorithm may be reapplied after refining λ^*. If this procedure takes excessive computational effort (more than 2 or 3 refits), the updating process is skipped ($H_{i+1} = H_i$) and the algorithm is continued as before.

(iii) <u>Cubic interpolation one-dimensional search technique</u>: Several methods are available for determining the optimum step length λ^* in the Eqn. $\vec{X}_{i+1} = \vec{X}_i + \lambda^* s_i$. The ultimate subroutine which deals with the function and minimizes the step lengths for optimum value of the objective function is this one-dimensional minimization routine. Hence an efficient method has to be chosen in order to improve the algorithm in getting best results. Out of various methods available, the cubic interpolation method is agreed to be the best one. This utilizes gradients which are being computed in case unconstrained variable matrix methods, hence the things previously computed are effectively utilized.

The minimizing step length is given by

$$\lambda^* = \lambda_B - \frac{\phi_B' + Q - Z}{\phi_B' - \phi_A' + 2Q}(\lambda_B - \lambda_A)$$

where

$$\phi(\lambda = \lambda_A) = \phi_A$$

$$\phi(\lambda = \lambda_B) = \phi_B$$

$$\left.\frac{\partial\phi}{\partial\lambda}\right|_{\lambda=\lambda_A} = \phi_A'$$

$$\left.\frac{\partial\phi}{\partial\lambda}\right|_{\lambda=\lambda_B} = \phi_B'$$

and $\quad \phi_A' < 0 < \phi_B'$

Also $\quad Z = \frac{3(\phi_A - \phi_B)}{B - A} + \phi_B' + \phi_A'$

$$Q = {Z^2 - \phi_A' \phi_B'}^{1/2}$$

The effort involved in this algorithm is reaching the points $\lambda = A$; $\lambda = B$ such that $\phi_A' < 0 < \phi_B'$. If the initial step length λ is very small it is given numerous increments necessary to reach the above condition. Or if the initial step length chosen is comparatively large provision is made to lessen the step length also.

The one-dimensional interpolation procedure is terminated when the cosine of the angle between $\vec{S}_i$ and $\quad \phi_{i+1}$ is small.

$$|\cos\theta| = \left| \frac{\vec{S}_i^T \cdot \nabla\emptyset_{i+1}}{|S| \ |\nabla\emptyset_{i+1}|} \right| < \epsilon$$

If this orthogonality test fails, the interpolation is again performed setting

$$\lambda_B = \lambda^*$$

$$\emptyset_B = \emptyset^*$$

$$\emptyset_B' = \vec{S}_i^T \nabla\emptyset_{i+1} \qquad \text{if} \quad \vec{S}_i^T \nabla\emptyset_{i+1} > 0.$$

Otherwise

$$\lambda_A = \lambda^*$$

$$\emptyset_A = \emptyset^*$$

$$\emptyset_A' = \vec{S}_i^T \nabla\emptyset_{i+1} \ .$$

5. THEORETICAL BACKGROUND OF OPTIMIZATION PROBLEM FORMULATION

5.1. General:

Clariflocculation has been proposed for investigation in the treatment of raw water for maximum tannin removal. Since the time of contact required is less and moderate agitation is expected to be sufficient, clariflocculation unit has been choosen so that there would be no need to go in for a new unit process requiring more finances.

5.2 Optimization Problem Formulation:

In the optimization of the clariflocculation the following variables were assumed to be taking most significant part and were considered in the formulation of the optimization problem.

(i) Raw water turbidity

(ii) Alkalinity of raw water

(iii) Velocity gradient

(iv) Time of flocculation.

To remove the tannin-loaded turbidity, a coagulant is necessary. Alum $(Al_2(SO_4)_3.16\ H_2O)$ has been choosen as the coagulant in the present work.

The objective of the work was to maximize the tannin removal, and hence experiments were conducted to evaluate various relationships with tannin removal as functions of velocity gradient, time of flocculation, turbidity and alum dose.

5.2.1 Objective function:

Kawamura (1967) proposed a relationship for the dose of coagulant in terms of raw water alkalinity and colloidal charge.

$$D = K_1 A + K_2 C^n \qquad \dots (5.1)$$

where

D	:	Dose of the coagulant, mg/l
C	:	Colloidal charge, meq./l
A	:	Total alkalinity, mg/l as $CaCO_3$
K_1, K_2, n	:	Constants.

A graphical method also was suggested to solve for K_1, K_2 and n. On the basis of their laboratory studies, Tekippe and Ham (1970) observed that the usefulness of this technique was dependent somewhat on buffering capacity of water. Also, it was thought that this technique would be more useful for suspensions with higher initial charges.

The constants of the Kawamura's equation were found out using the experimental results on alum doses with different colloidal charges. Kawamura determined the constants for maximum turbidity removal. In the present work the turbidity, in place of colloidal charge, has been used since a definite relation exists between these two. In case of the present work, it is proposed to find the constants for maximum removal of tannin loaded turbidity using graphical method outlined by

Kawamura (1967). The appropriate data could also be fed to the computer in the nonlinear regression analysis algorithm (explained in Chapter 4) to evaluate the constants. A comparison of these would be done in Chapter 6.

Hence it has been proposed to select the dose of alum for the maximum removal of tannin loaded turbidity as the primary objective and the objective function can be written as below.

$$D = K_1 A + K_2 B^{k_3} \qquad \dots (5.2)$$

where

D : Dose of alum, mg/l

A : Alkalinity, mg/l as $CaCO_3$

B : Raw water turbidity loaded with tannin or surface provided for adsorption of tannins.

According to O'Melia (Weber, 1972), the agitation accelerates the aggregation of particles. In such systems, the velocity of the fluid varies both spatially (from point to point) and temporarily (from time to time). The spatial changes in velocity have been characterised by a velocity gradient, G. Particles which follow the fluid motion will also have different velocities, so that opportunities exist for interparticle contacts. When contacts between particles are caused by fluid motion, the process is generally termed as 'orthokinetic flocculation' (Overbeek, 1952).

This can be mathematically described as

$$B = B_0(1 - e^{-\emptyset Gt})$$

where

B : Turbidity at any time 't'

B_0 : Initial turbidity

$\emptyset$: A constant

G : Velocity gradient

t : Time of flocculation.

The above equation relates the effect of Gt to the residual turbidity according to 'orthokinetic flocculation'. This Gt-factor, a nondimensional parameter is widely used in the flocculator designs.

5.2.2 Constraints for the objective function:

The process being very simple, only side constraints are sufficient in obtaining the optimum solutions. These are as follows.

5.2.2.1 Alkalinity ('A' measured as mg/l as $CaCO_3$): The alkalinity of raw water is considered to be one of the most influencing factors in alum coagulation. Alkalinity provides buffering capacity to water and thus the pH reduction is negligible on addition of alum. Alkalinity would keep the pH of water in a range (6.0 to 7.8) favourably for alum coagulation to achieve the maximum removal of tannin loaded turbidity.

Kawamura (1967) stated that it can be conveniently assumed /that the behaviour of alkalinity is exactly same as that of the turbidity. The constraining values have been found on the experience of natural river water alkalinities and are shown below:

$$20 \leq A \leq 800 \qquad \qquad \ldots (5.3)$$

5.2.2.2 Turbidity ('B' measured as N.T.U.): The turbidity value is fed as the available data and other conditions for optimum removal were obtained in a few sets of results. However, one set has been tried considering turbidity also as a variable for which the constraint is:

$$1 \leq B \leq 1000 \qquad \qquad \ldots (5.4)$$

5.2.2.3 Velocity gradient ('G' measured as sec^{-1}): The limitations have been given by O'Melia (Weber, 1972) and are shown below:

$$10 \leq G \leq 100 \qquad \qquad \ldots (5.5)$$

5.2.2.4 Time of flocculation ('t) measured as seconds): The limitations were fixed from the knowledge of normal times of flocculation followed in water treatment plants:

$$0.1 \leq t \leq 1800 \qquad \qquad \ldots (5.6)$$

6. RESULTS AND DISCUSSION

General:

This study is mainly planned to evolve the criteria for maximum tannin removal in conventional water treatment plants with as little number of process modifications as possible so as to avoid additional expenses of having new process units. The study has been done in three different phases.

(i) Phase I : Studying the potential of natural turbidity for the sorption of tannins.

(ii) Phase II : Evaluation of the conventional coagulation process for removal of tannin loaded turbidity, introducing process modifications for maximizing the removal and also evolving relationships between tannin removals and parameters influencing the process.

(iii) Phase III: Optimizing the various parameters involved in the process for maximum removal of tannins using nonlinear programming techniques.

The results obtained in the different phases are presented and discussed as under.

6.1 Phase I:

In this phase of study, natural turbid waters were drawn from lower Ganga canal located near I.I.T. Kanpur. It was found that tannins were not present in the canal water. In this phase of study, two sets of experiments were conducted.

Set I : Keeping turbidity as constant and varying initial tannin concentrations.

Set II: Initial tannin concentration kept constant and varying the turbidities.

To the natural water having a turbidity of 140 NTU, tannins were added to simulate tannin concentrations present in the river waters. Experiments using jar test apparatus were conducted to transport tannins from the bulk to the surface of turbid particles. The turbid particles were spun down in the centrifuge and tannin was estimated in the supernatant. Figure 6.1 shows the observed isotherm for tannin removals for the simulated canal water. Figure 6.2 shows the Freundlich's linearization of the observed isotherm. It can be seen that the linearized plot is a straight line and appears to follow the Freundlich's isotherm. Freundlich's equation (Weber, 1972) is basically empirical but is often useful as a means of data description. The equation in a general form is

$$q_e = K_F \, C^{1/n} \qquad \qquad \ldots (6.1)$$
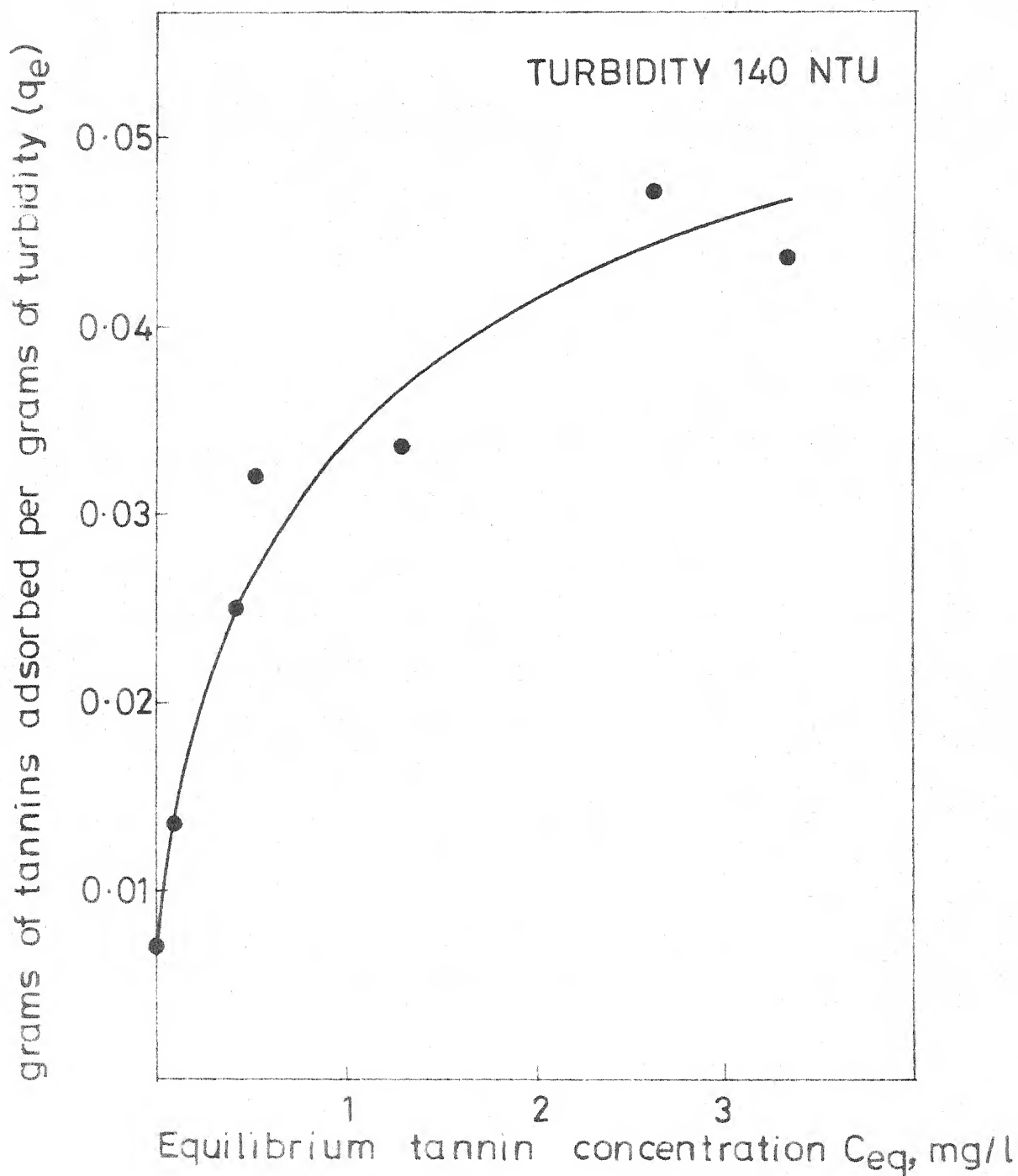
Fig. 6·1 Tannin   adsorption on natural
           turbidity as a function of initial
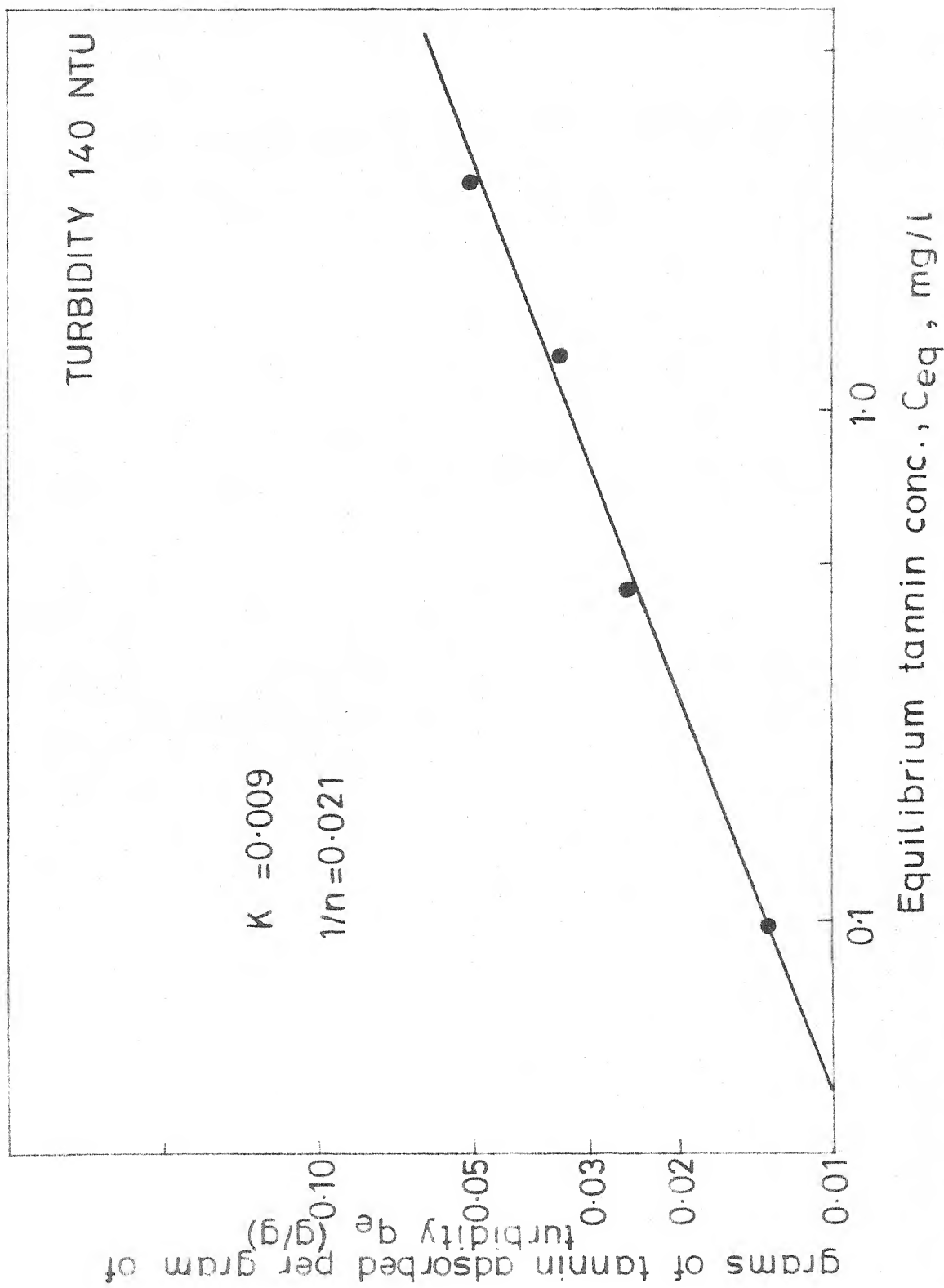   tannin concentrations.

Fig.6·2 Freundlich isotherm for tannin sorption on turbidity

where

q_e :   Grams of adsorbate per gram of adsorbent

K_F, n :   Freundlich's constants

C   :   Equilibrium concentration of adsorbate.

Freundlich equation is commonly used for the comparison of different powdered activated carbons for treatment. The logarithmic form of equation (6.1) applied to P.A.C. looks like

$$\log \frac{C_o - C}{D_o} = \log K_f + \frac{1}{n} \log C \qquad \ldots (6.2)$$

where

C_o :   Initial concentration of the contaminent

C   :   Concentration of the contaminent at time 't'

D_o :   Dosage of P.A.C.

In the second part, the tannin concentration in the canal water was kept constant and turbidities were varied. In order to obtain test water with different turbidities, the canal water was diluted approximately with turbid free canal water. The turbid free canal water was prepared by centrifugation. The samples, with varying surface (turbidity), were subjected to jar test with the addition of alum. The results regarding tannin removal as a function of turbidity, were presented in Figure 6.3.

The values from the figure show a steep increase in the tannin removal during the initial increases of turbidity
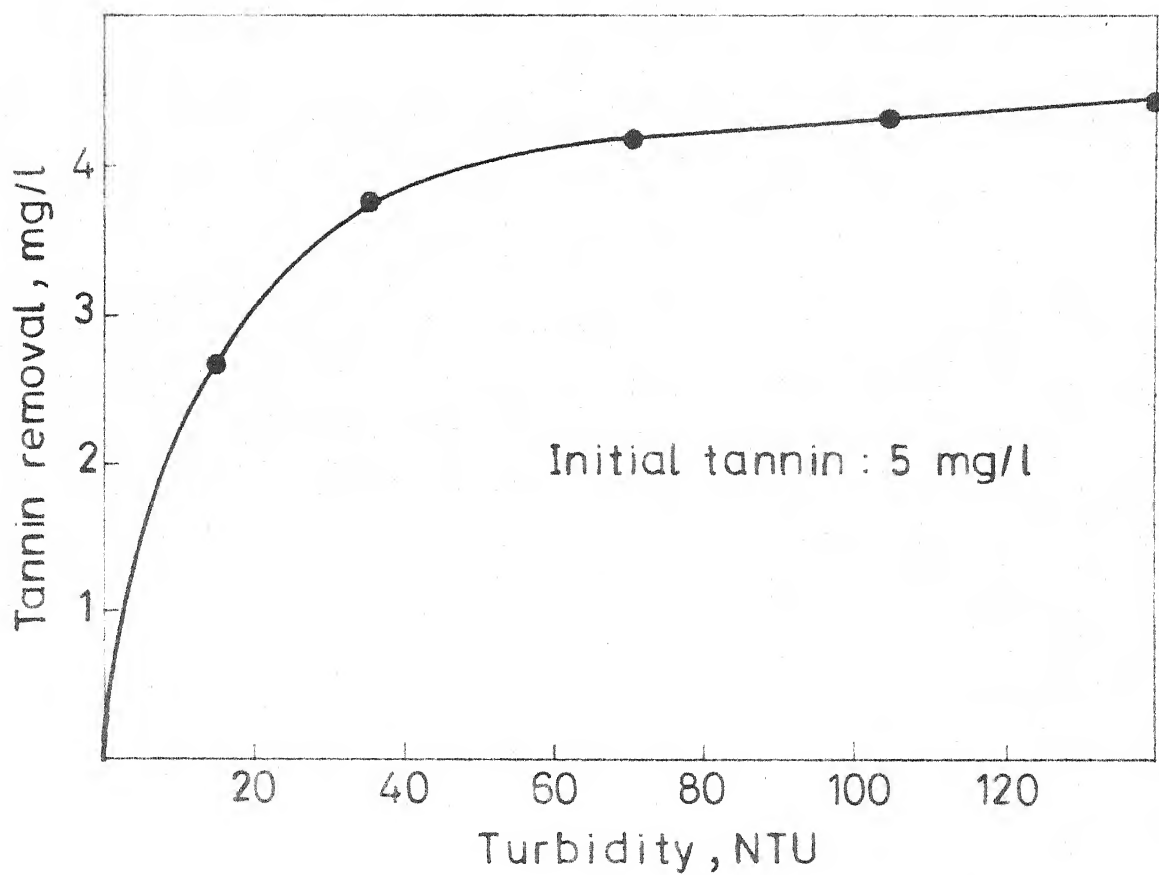
Fig. 6·3 Tannin removal as a function of natural turbidity

but it seemed later that an optimum turbidity value could easily be obtained showing that there would be a saturation level for the tannin removal. It can be seen that when tannins obtain the required surface for adsorption in the form of turbidity for maximum removal, further increase in the surface area is of no avail.

The river water containing tannins which serve many industries enter the concerning industry's water treatment plant. Since the river water is directly responsible for the tannin removal, it is to be investigated further to suggest certain process modifications for the removal of tannin loaded turbidity since it has already been seen that the tannin is adsorbing onto the turbidity of river waters. The results presented indicate that the natural turbidity of river waters has significant potential to adsorb the tannins discharged by tanneries into the water bodies. High tannin removal of the order of 85 percent can be obtained with a turbidity of 70 NTU. In most part of the year the turbidity of raw water in Ganga at Kanpur varies in the range of 65-220 NTU and during monsoon period, the turbidity is rather higher than these values (Ranade, 1976). Hence turbidity does not seem to be limiting step in tannin removal.

The raw water containing tannin loaded turbidity is treated in the water treatment plant of the industry. The treatment processes, viz., alum coagulation and flocculation,

sedimentation, and filtration should be efficient to remove
tannins and turbidity. In the succeeding sections, results
of investigations carried out to evaluate the tannin removals
by alum coagulation are presented. Further, slight process
modifications were incorporated to maximize the removals.

6.2 Phase II:

6,2.1 Assessment of clariflocculation to remove tannin loaded bentonite turbidity:

In this phase, the coagulation and flocculation
processes have been evaluated for the tannin removal. The
units are normally designed to remove major part of turbidity
present in raw water. Alum is most commonly used coagulant.
During coagulation, the alum added, causes the destabilisation
of the colloidal particles constituting the turbidity, and
induced velocity gradient in the flocculator causes the inter-
particle contacts resulting in the formation of aggregates
which settle down at a faster rate in the sedimentation tank.
Experiments conducted using tannin free bentonite turbidity
indicate that the optimum dose of alum for maximum removal of
turbidity depends upon the initial turbidity. As the turbidity
increases the required alum is less since transport (floccu-
lation) step is not rate limiting. The optimum alum doses for
15, 55 and 120 N.T.U. turbidities are respectively 200, 80
and 60 mg/l. The possible mechanism of destabilisation
appears to be adsorption of colloid particles on the polymer

hydroxometal complexes of alum which are formed during the reaction rather than enmeshment of turbidity in metal hydroxide complex.

In order to find out the effect of tannin loading on the turbidity and its removal by alum coagulation, jar test experiments were conducted using test water containing tannin loaded turbidity. Two sets of experiments were conducted in which initial tannin loading is 10 mg/l and 15 mg/l and three different turbidities used were 15, 55 and 120 N.T.U. The results on tannin removals for different alum doses are presented in Figures 6.4 and 6.5. It is evident that as initial turbidity increased the tannin removal increased. To obtain high removal of the order of 90 percent around 200 mg/l of alum dose was required while corresponding to 120 N.T.U. turbidity the dose of alum is less than 50 mg/l. Comparing the results of optimum alum doses for removing tannin free turbidity with the present results, one can draw an important inference that there is no difference in coagulation of tannin loaded and tannin free turbidity. However, the limiting step in the case of tannin removal also appears to be flocculation. If the initial turbidity is higher, lesser alum doses are required for the same tannin removal. It was pointed out in Phase I that in most part of the year the turbidity of Ganges water is around 100 N.T.U. and hence very significant tannin removals can be achieved by adopting the identical dose of alum to remove tannin free turbidity. However, in summer
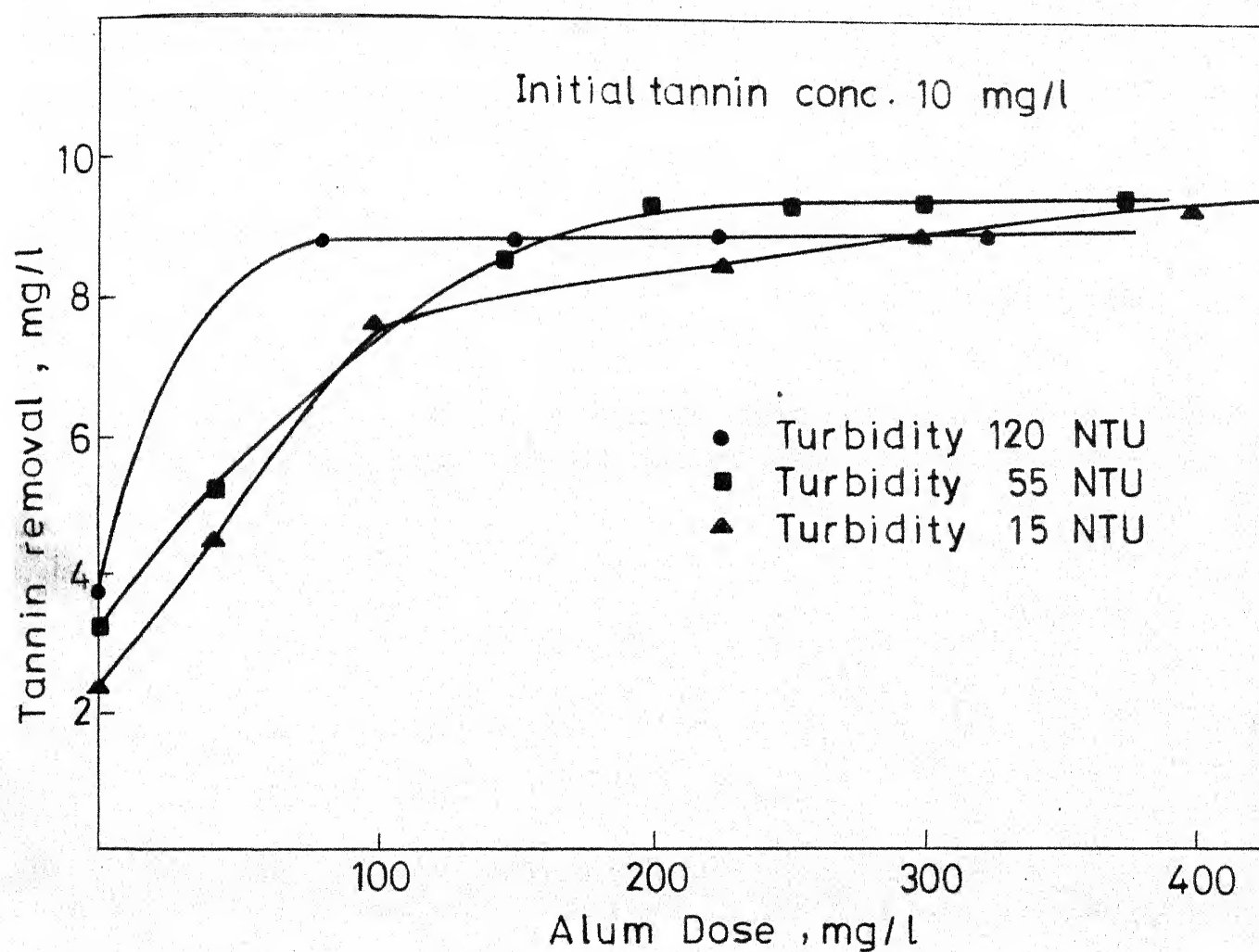
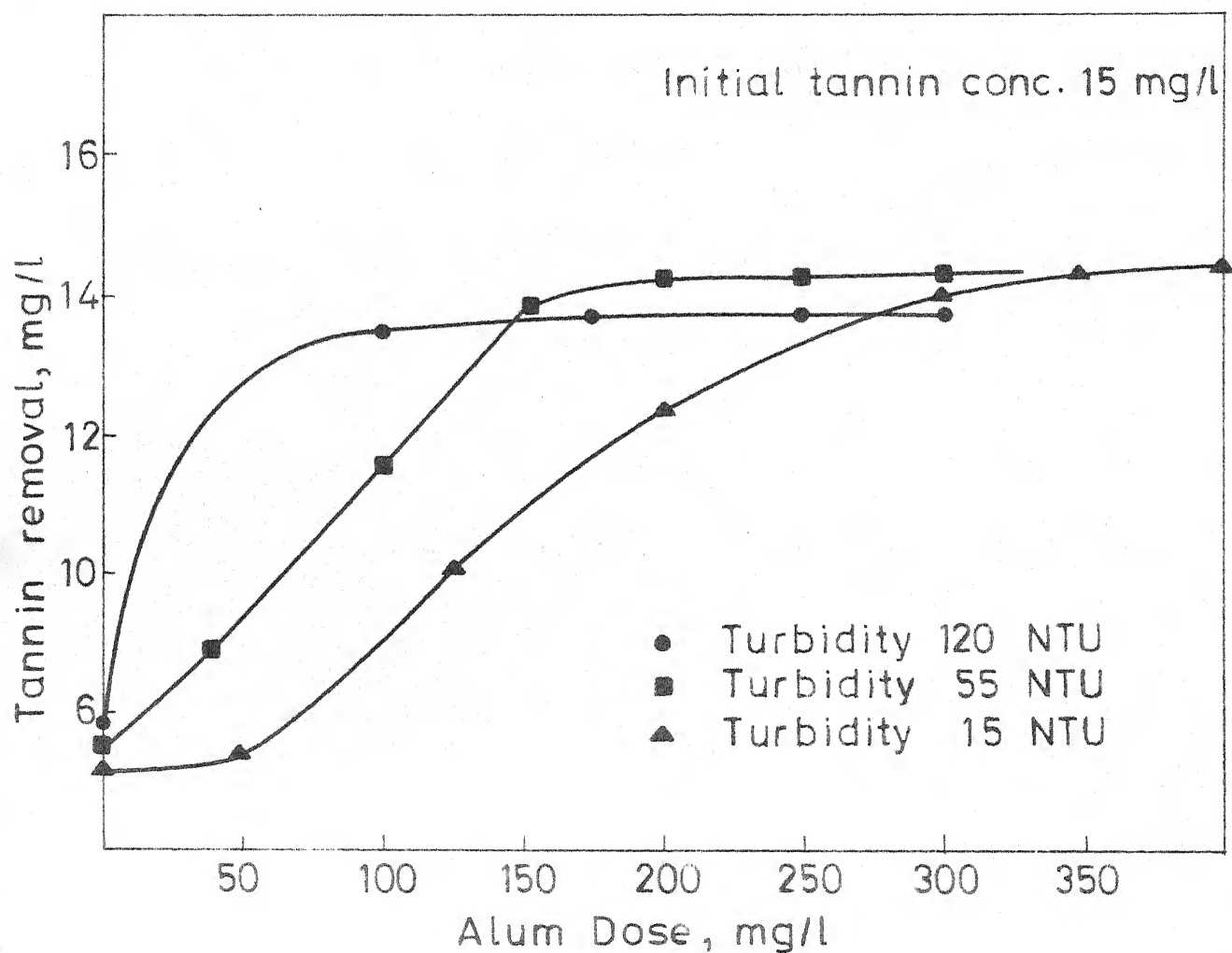Fig. 6·4 Tannin removal as a function of Alum Dose (Set-I)

Fig. 6·5 Tannin removal as a function of Alum Dose

(Set-II)

months when the turbidity is less than 65 N.T.U. higher doses of alum are required. In the present investigation the induced velocity gradient (G) was calculated by knowing power input to system and volume of water treated according to the equation

$$G = (\frac{P}{V\mu})^{0.5} \qquad \qquad ...(6.3)$$

In the jar test apparatus the interparticle contacts are achieved by means of rotary paddles and induced G value in these experiments to be 30 sec^{-1} and Gt factor was 35,500. In the conventional water treatment plants the normal range of Gt factor is 12,000 to 1,20,000.

Utilizing the same data, isotherms were plotted to know about the sorption of tannin taking place on turbidity and alum floc. Freundlich's isotherm equation seemed to be the best fit for the data signifying the heterogeneous behaviour of the adsorption process. The Freundlich's linearized isotherms drawn for systems with and without alum doses are presented in Figures 6.6 and 6.7.

Recollecting the behaviour of the Freundlich isotherm in case of natural turbidity in Figure 6.2, it can be said that the bentonite turbidity loaded with tannin is exhibiting similar results. In the present section, alum coagulation has replaced the centrifugation of the previous section. There is a significant resemblance between powdered
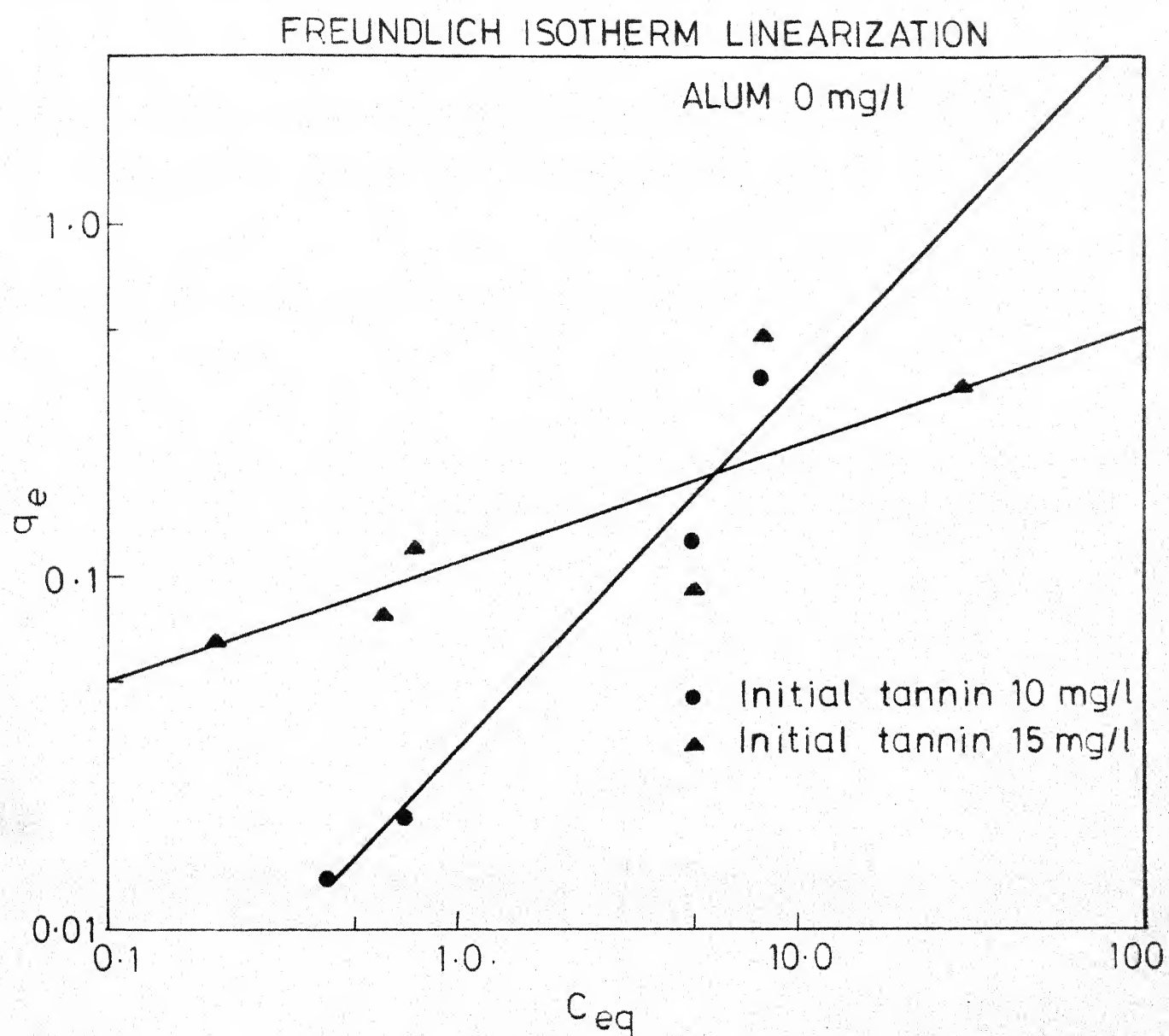
FREUNDLICH ISOTHERM LINEARIZATION

ALUM 0 mg/l

Initial tannin 10 mg/l
Initial tannin 15 mg/l

Fig. 6·6 Tannin removal on artificial turbidity
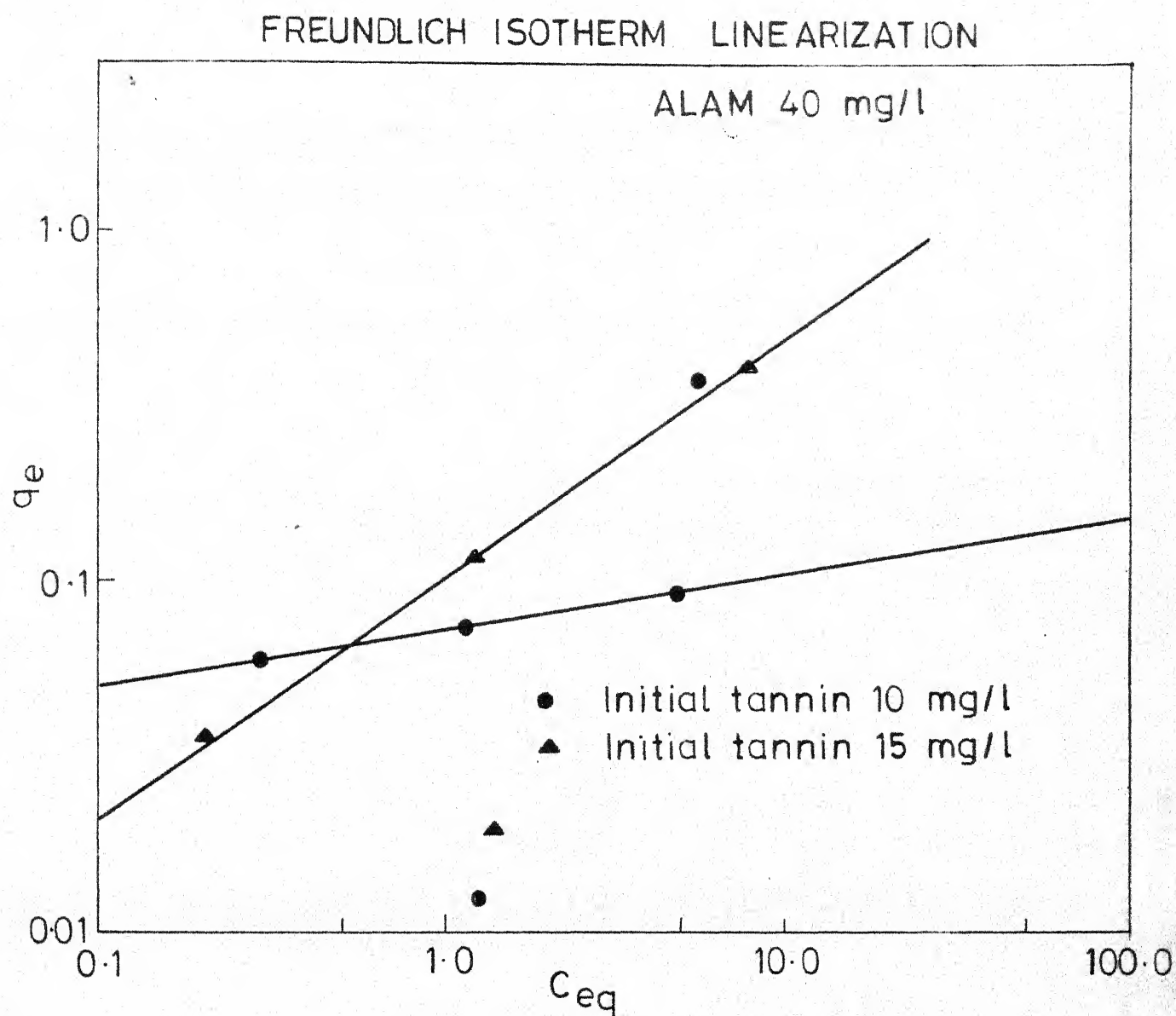
FREUNDLICH ISOTHERM LINEARIZATION

Fig. 6·7 Tannin removl aided by Alum coagulation

activated carbon and turbidity present in water in terms of
particle size and surface area offered for sorption. The
surface area of bentonite is 425.61 m^2/g which is reasonably
a high value, though lesser than that of active carbon whose
surface area would be about 1000 m^2/g. Mostly the powdered
activated carbon in water treatment follow the Freundlich's
equation (Weber, 1972). It was rather expected that the
data regarding tannin sorption on the river water turbidity
also follows the Freundlich isotherm similar to P.A.C.
behaviour.

The Freundlich's constants K_f and $1/n$ give an
estimate of the amount of sorption and adsorption intensity
for tannin loaded bentonite turbidity coagulated with alum,
the value of K_f is observed to be higher than that coagulated
with 0 mg/l of alum dose. It is clear from Figures 6.6 and
6.7 that the increase in K_f is from 0.002 to 0.015 for an
initial tannin concentration of 10 mg/l. This clearly shows
that the surface available for sorption of tannins increased
due to alum flocks besides bentonite turbidity, appear to
contribute additional surface area for sorption of tannins.

6.2.2 Influence of 'Gt' factor on tannin loaded bentonite
       turbidity removals:

It was mentioned earlier that alum coagulation and
flocculation can conveniently be used for tannin removal
without further modifications during the monsoons and high

turbidity period. However, high alum dose is required during summer months since turbidity of river water is low. In order to reduce alum dose for concurrent removals of tannins and turbidity, efforts are made to study these removals at different induced velocity gradients and flocculating times. This would lead to evaluate an optimal 'Gt' factor to achieve maximum removals of tannins and turbidity keeping the alum dose as low as possible.

A series of jar tests were conducted to study the effects of G and t or 'Gt' factor. Varying the velocity gradients for different times of flocculation, the experiments were conducted with 5, 10 and 15 mg/l of initial tannin concentrations. However alum doses were kept approximately optimum to coagulate the tannin loaded turbidity. The information regarding optimum alum dose was obtained in the earlier stages of the study. The results are shown in Figures 6.8, 6.9 and 6.10 drawn for different values of turbidity.

Results presented in the figures indicate that there exists an optimum 'Gt' factor for maximum removal of tannins. If the 'Gt' factor increased beyond this optimum value the removal of tannins decreased and this may be due to the shearing of alum flock which results in dispersion of tannins in the solution. The optimum 'Gt' factor appears to be same irrespective of initial tannin concentrations for a particular turbidity and this indicates that 'Gt' is
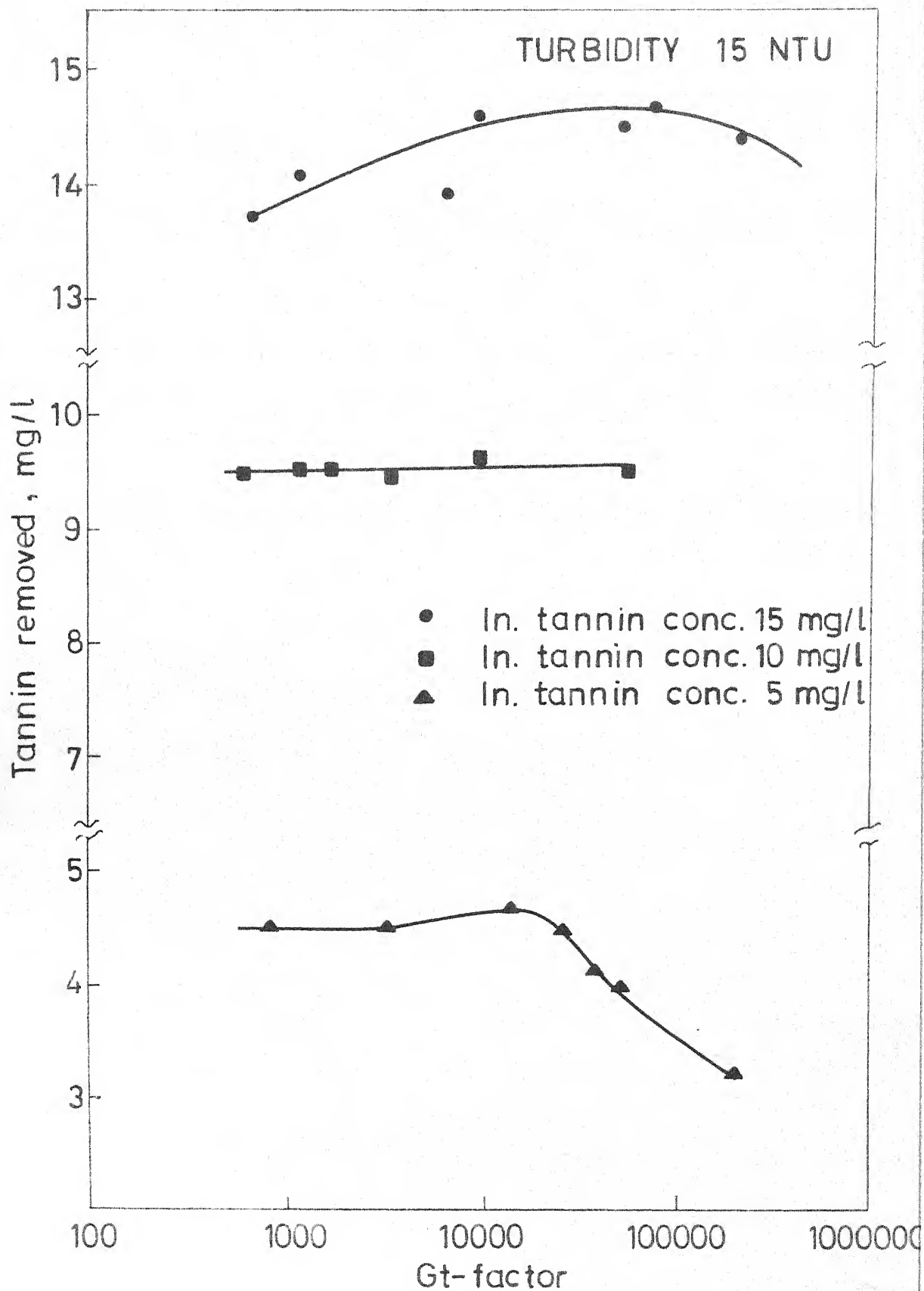
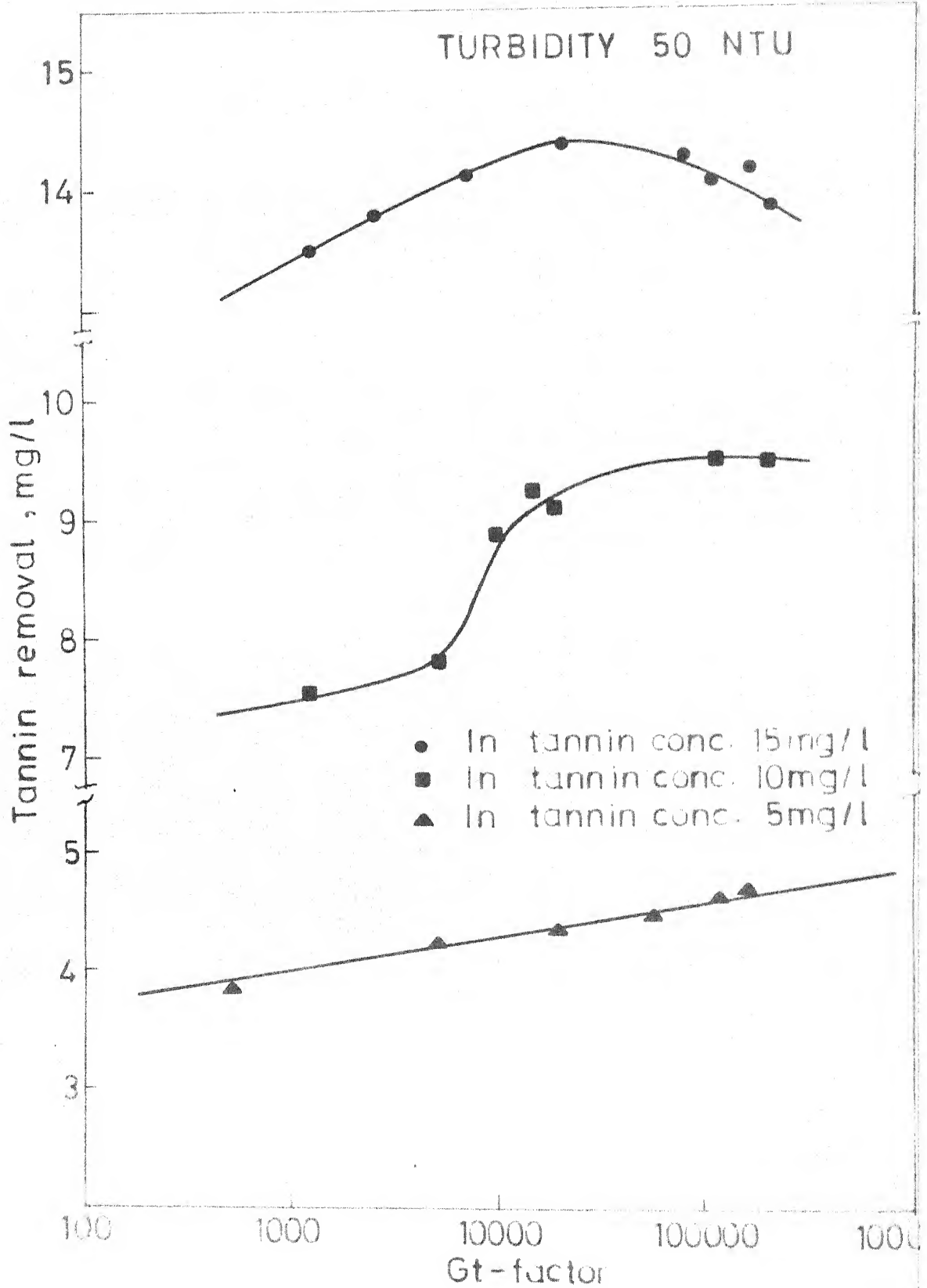Fig. 6·8 Tannin removal as a function
of Gt-factor
(Set-1)

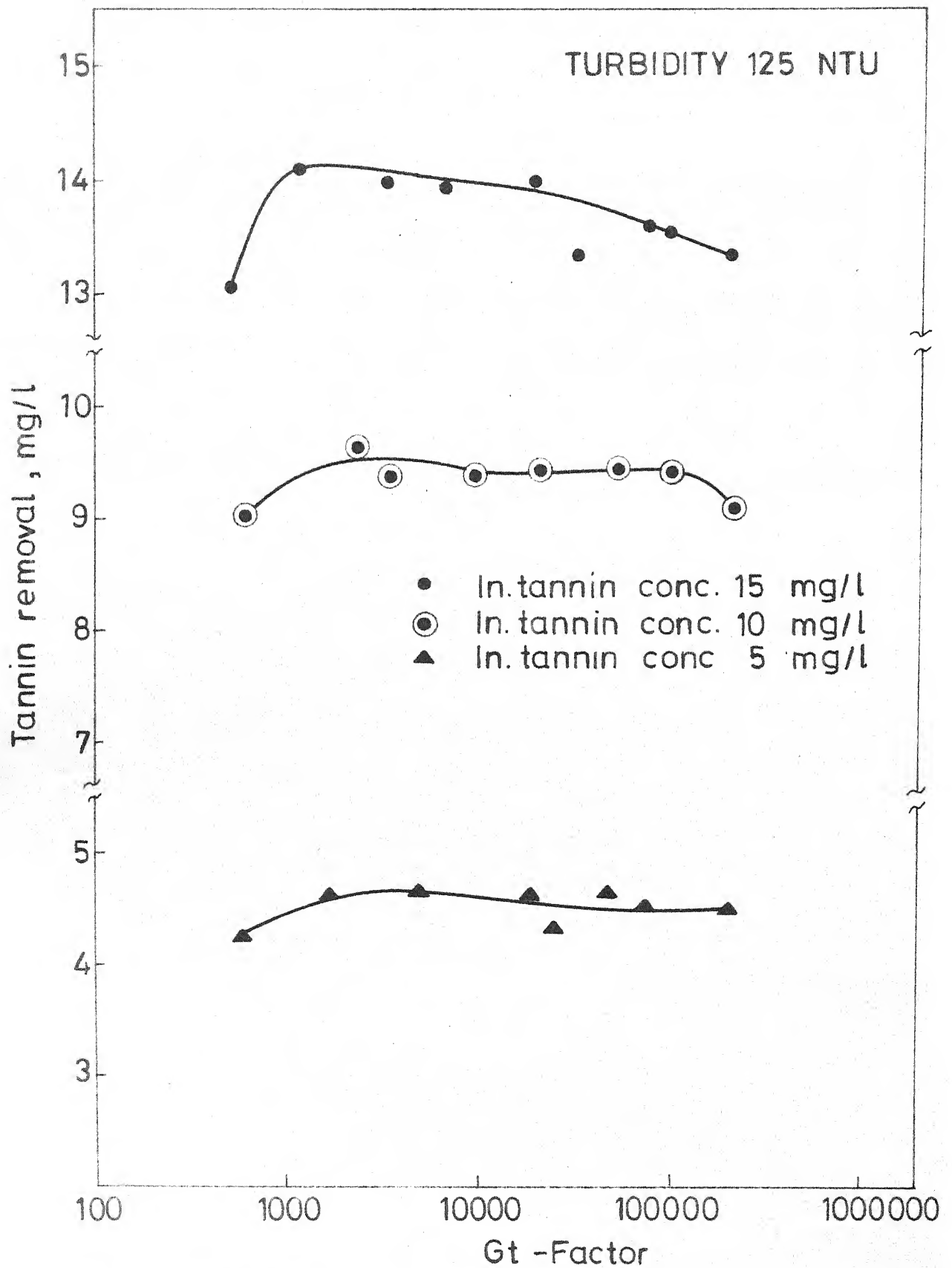Fig. 6·9 Tannin removal as a function Gt-factor

Fig. 6·10 Tannin as a function of Gt-factor
(Set-III)

independent of initial tannin loading on turbidity. However, from Figure 6.8 it can be seen that there is no clear cut optimum for 10 mg/l of tannin loading onto 15 N.T.U. bentonite turbidity while other two curves exhibit some sort of optimum 'Gt'. Again from Figure 6.9, similar observations for 5 mg/l of tannin loading onto 50 N.T.U. turbidity can be seen. Although the reason for this behaviour is not known, observations exhibit a trend.

However, the comparison of optimum Gt values for various turbidities indicate that as the turbidity increases, the optimum 'Gt' value decreases. The data presented in Figure 6.11 clearly indicates this aspect for a 90 percent tannin removal with various initial tannin concentrations. This can lead to the inference that optimum Gt is dependent upon the turbidity of raw water and tannin loading does not have any significant effect. For an initial tannin concentration in raw waters of 15 mg/l and a turbidity of 125 N.T.U., the optimum 'Gt' to be provided is 1000 sec^{-1} for an optimum alum dose or about 90 percent tannin removal. As the turbidity of raw water decreases, the Gt-factor increases very rapidly resulting in the increase of the cost of flocculation.

The optimum Gt, 1000 sec^{-1}, can be provided by optimizing both velocity gradient, G and residence time, t, in the flocculation. Assuming G to be 30 sec^{-1}, the contact time in the flocculation can be calculated to be less than
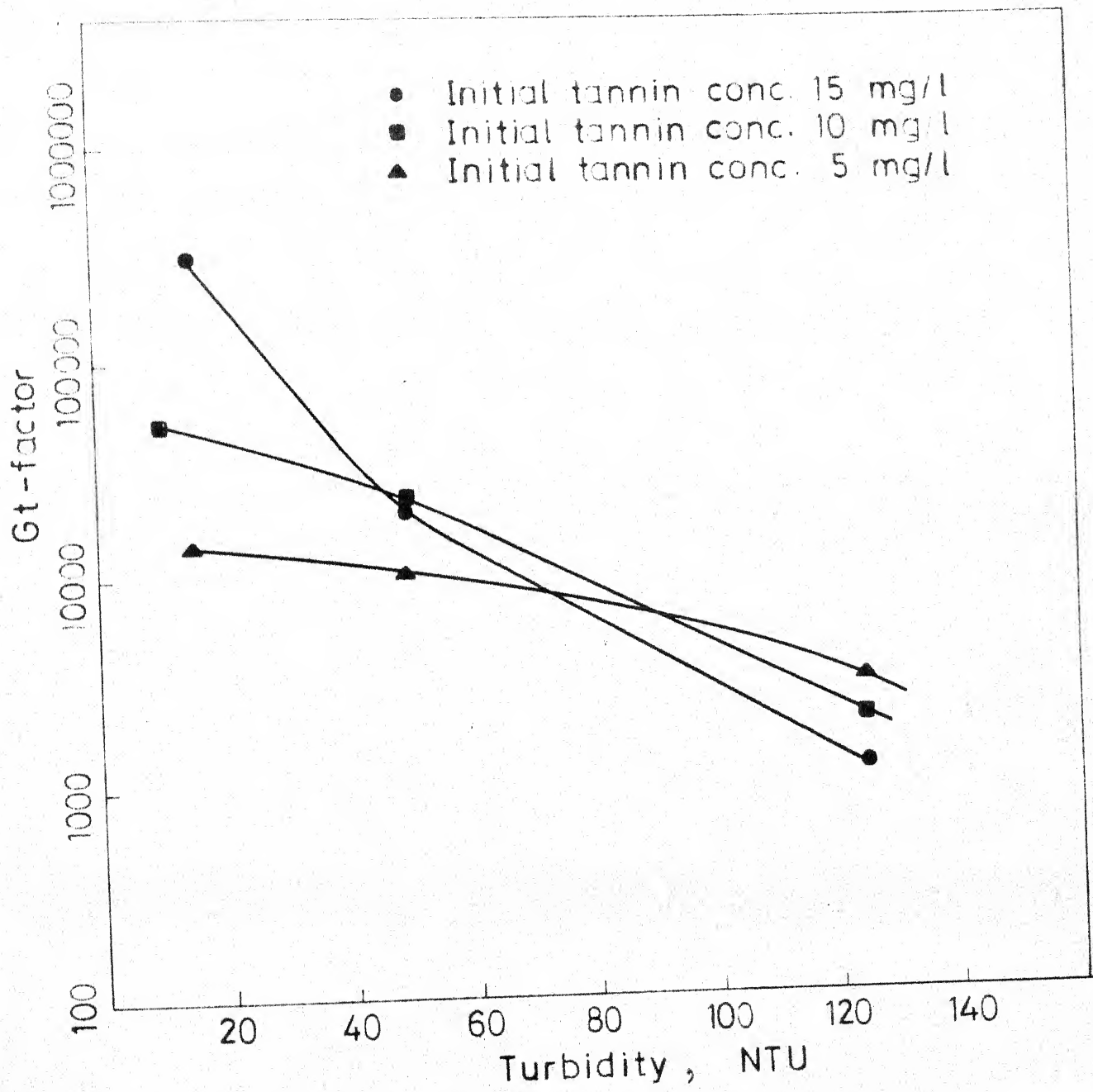
Fig. 6·11 Variation of optimum Gt-factor with turbidity

a minute. If the turbidity of raw water is decreased to 60 N.T.U., then the optimum 'Gt' value is 12,000 and accordingly the time of flocculation is found to be 7 minutes. However, in practice, a constant residence time is provided in the flocculator and means that value increases for lower turbidities for obtaining some tannin removal. Increase in G value results in more power consumption and hence more cost. Moreover, G values cannot be increased indefinitely otherwise the high velocity gradients shear off the flocs defeating the purpose of flocculation. Hence the turbidity of raw water should not be low for maximum tannin removal and in such situations, it is not strange even to add bentonite clay to water to increase the turbidity.

However, an alternative to handle the raw waters having low turbidity is by increasing the alum dose such that sweep flocs are formed due to formation of metal hydroxide precipitate. The precipitate provides the desired surface for the tannin adsorption besides low turbidity. This would involve in more consumption of alum and hence increases the cost.

6.3 Phase III: Optimization of the Parameters Influencing the Tannin Removals:

6.3.1 Evaluation of the constants of Kawamura's equations:

The data obtained in removal of tannin loaded turbidity by alum coagulation and flocculation in the Phase II

is utilized to find the constants in the following objective
function.

$$D = K_1 A + K_2 B^{K_3} \qquad \ldots (6.4)$$

This can be written as

$$(D - K_1 A) = K_2 B^{K_3} \qquad \ldots (6.5)$$

or $$\log (D - K_1 A) = \log K_2 + K_3 \log B \qquad \ldots (6.6)$$

By plotting a graph $(D - K_1 A)$ Vs. B in a log-log
plot, the constants K_2 and K_3 can be found out from the
properties of the straight line obtained. But K_1 being an
unknown, a trial and error procedure has been adopted. In
this procedure, for a trial value of K_1, the $(D - K_1 A)$ Vs. B
relation was plotted utilizing the existing experimental
data. If this plot is not a straight line, the value of K_1
assumed must be wrong. This procedure is repeated until the
plot gives a straight line. The value of K_1 assumed in the
final trial is the actual value of K_1. The constants K_2 and
K_3 are evaluated from the equation of the straight line
obtained. Figure 6.12 depicts the various trials made, and
the constants, both when turbidity is less than 100 N.T.U.
and greater than 100 N.T.U. These constants can also be
obtained using nonlinear regression analysis (a modified
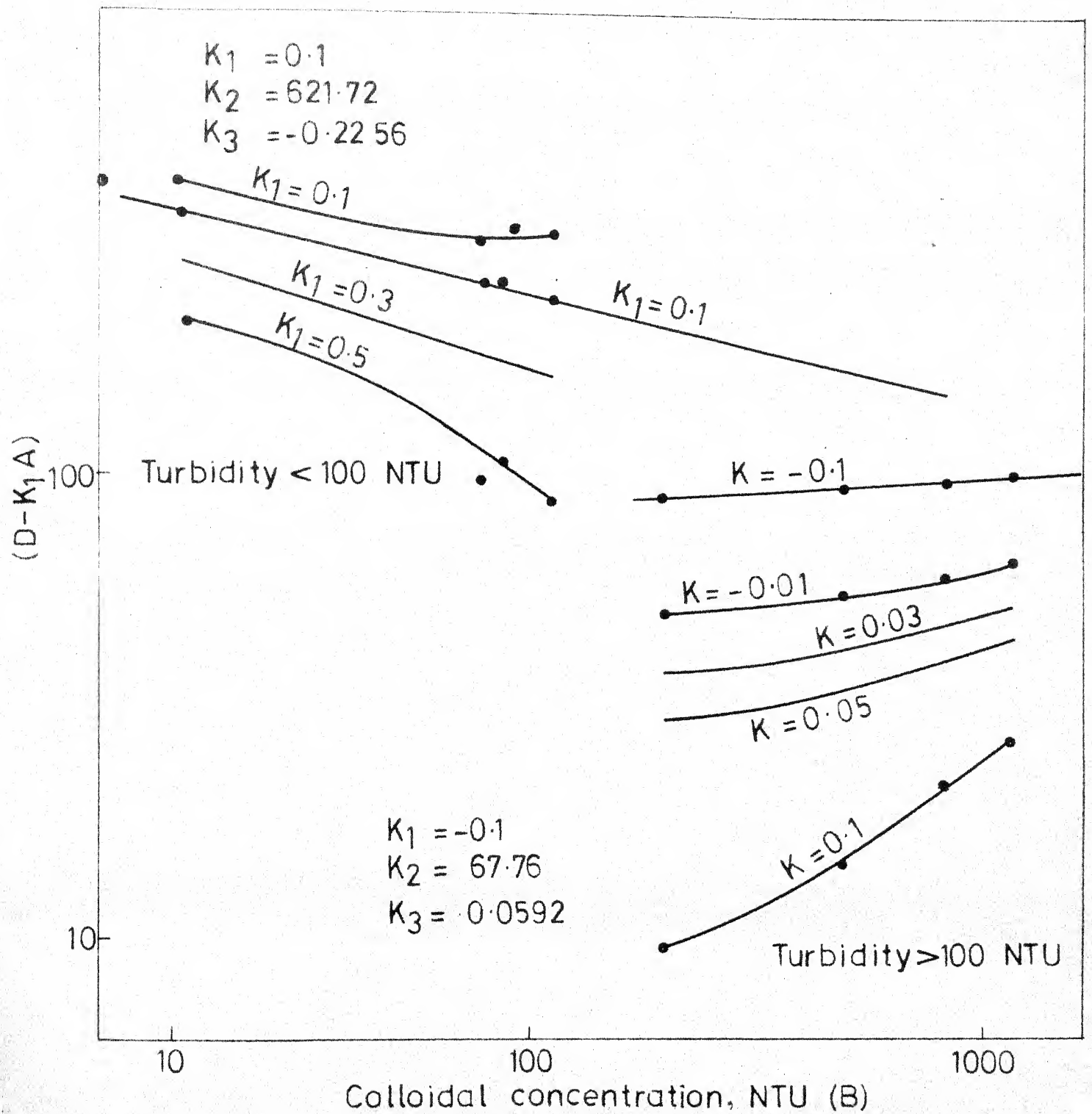version of the linear regression explained in Chapter 4).

Fig. 6·12 Evaluation of constants in $D = K_1 A + K_2 B^K$

Verma (1975) while using this Kawamura's equation found out the constants for the lower Ganga canal water for maximum turbidity removal are for colloidal charge

$$C < 100 \text{ meq/l} \qquad D = 0.5 A + 0.55 C^{1.08}$$

$$100 < C < 200, \qquad D = 0.5 A + 80 C^{0.0}$$

$$C < 200 \qquad , \qquad D = 0.65 A + 0.55 C^{0.88}$$

A comparison of the values obtained from Figure 6.12 with those of Verma (1975) reveals that there is a significant difference in the constants. This is because the systems are different. The effect of alkalinity on the tannin removal is seen very less when compared to that in case of turbidity removal. However, turbidity removal is also associated with the tannin removal since alum is employed to remove tannin-loaded turbidity. The constants derived from both regression analysis and graphical method are presented in Table 6.1.

<u>Table 6.1</u>

Kawamura's Constants

Constant	B(Bentonite turbidity) 100 NTU		B(Bentonite turbidity 100 NTU	
	Graphical analysis	Regression analysis	Graphical analysis	Regression analysis
K_1	0.10	0.1084	-0.10	-0.1096
K_2	621.72	632.574	67.76	64.34
K_3	-0.2256	-0.224	0.0592	0.0578

From the Table 6.1, it is seen that the values from the computer are quite agreeing with the values calculated from graphical method. Hence for a meaningful interpretation, the values may be computed from the nonlinear regression. However, it is better to verify the deviations in the initial trials from the graphical values.

The constant so obtained show that the process is not highly dependent on alkalinity. The constants seem to be dependent upon the turbidity when maximum tannin removal is considered. As the turbidity changes, a significant difference has been observed in the values of the constants.

6.3.2 Optimization of the problem:

An efficient nonlinear programming algorithm was developed as presented in Chapter 5. 'Fortran-IV' language is utilized in the programming. The computer used was DEC-1090 (Maynerd, Mass., U.S.A.).

The optimal conditions for maximum removal of tannins from the raw waters of a given turbidity can be obtained using the algorithm. The results obtained using the developed algorithm are presented in Table 6.2. For different combinations of raw water turbidities and initial tannin concentrations, the optimal values for alkalinity, alum dose, velocity gradient, and flocculating time are obtained and be seen in Table 6.2. The tannin removals are also, however, presented.

Table 6.2

Results from Optimization Algorithm

Sr. No.	Turbidity NTU	Alum dose mg/l	Alkalinity mg/l as $CaCO_3$	Velocity gradient sec^{-1}	Time of flocculation seconds	Initial tannins mg/l	Final tannins mg/l	% removal
1	50	292.0	341.0	25.7	898	10	2.35	76.50
2	50	302.4	359.0	35.6	954	15	2.00	86.67
3	100	76.2	127.5	2.27	883	10	1.30	87.00
4	100	81.1	148.4	15.8	1196	15	1.40	93.33
5	104.64	71.1	321.3	12.4	1864	10	1.05	89.50

The difficult task of finding the final concentration of tannins has been done by interpolating the existing experimental data for tannin removals with different turbidities and alum doses. Lagrangian interpolation method described in Chapter 4 has been used for the purpose.

The first four columns indicate the optimal conditions for given initial tannin-turbidity combinations. These are seemed to be quite meaningful while comparing with the actual experimental results in case of tannin removals. It is also clear that optimal conditions viz., velocity gradient, time of flocculation alum dose and alkalinity found from the optimization problem promote the saving in case of the operational cost.

When turbidity was also taken as a variable, the values obtained are shown in item 5 of the Table 6.2. This shows that the turbidity around 100 N.T.U. will be best for tannin removal in the coagulation and flocculation unit to indicate a removal of about 90 percent of tannin.

7. CONCLUSIONS

Based on the experimental work the following conclusions may be drawn:

(1)   Natural river water turbidity is very effective in removing tannins from river water.

(2)   Stable bentonite clay suspensions also adsorb tannins effectively.

(3)   Coagulation and flocculation effectively remove tannin and turbidity concurrently.

(4)   Greater alum doses are required for tannin removal in case of low turbidities and vice versa for a particular initial tannin concentrations.

(5)   Both tann-natural turbidity and tannin-bentonite turbidity systems exhibit Freundlich isotherm.

(6)   Alum flocs also provide extra surface for the sorption of tannins besides turbid particles.

(7)   The 'Gt' factor is a very important parameter in the removal of tannins and turbidity and is mostly on the raw water, turbidity value. As turbidity decreases the optimal Gt factor rapidly increases for maximum tannin and turbidity removal.

(8)   Using the interior penalty function method the process can be conveniently optimized for optimal values of the parameters influencing the process, viz., alum dose, velocity gradient and time of flocculation.

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